

Microscale Zn Speciation in a Smelter-Contaminated Soil

D.R.Roberts¹, A.C. Scheinost², G.M. Lamble³ and D.L. Sparks¹

¹Dept. of Plant and Soil Sciences, University of Delaware, Newark, DE 19717

²Institute of Terrestrial Ecology - Soil Chemistry. Swiss Federal Institute of Technology Zurich (ETHZ)
Grabenstrasse 3 CH-8952 Schlieren, Switzerland

³Advanced Light Source, Ernest Orlando Lawrence Berkeley National Laboratory,
University of California, Berkeley, CA 94720, USA

INTRODUCTION

The introduction of heavy metals such as Cd, Ni, Pb, and Zn into soils as a result of mining and smelting operations may result in detrimental effects to plants, soil organisms, wildlife, and livestock. Ultimately these metals may reach human populations where they pose the threat of being toxic. The fate of potentially toxic metals and their potential for human exposure is greatly dependent on the speciation of the metal in soils. Traditionally, the speciation of metals in soils has been achieved using indirect methods such as sequential extraction techniques or modeling based on thermodynamic data obtained in laboratory studies. While these approaches are useful in determining major chemical species and the average speciation within a sample, the results are difficult to interpret in complex soil samples [1]. The advent of high-brilliance X-ray sources such as the Advanced Light Source (ALS) and its combination with X-ray microfocussing optics has resulted in a tool which can aid in direct identification of metal species in contaminated soils [2].

The historic smelting facility in Palmerton, PA has resulted in the introduction of Cd, Pb, and Zn emissions into the vicinity around the site. One area which was severely devastated was the Blue Mountain operable unit consisting of 2,000 acres on the north slope of Blue Mountain. Revegetation efforts began in 1991 and currently half of the 2,000 acres have grass cover. The other half of the mountain has limited vegetative growth so soil erosion continues to be of great concern. The heavy Zn deposits have resulted in Zn concentrations in the percentage range. The Zn was introduced into the soil as small particles of the mineral franklinite (ZnFe_2O_4). Once on soil surfaces, metal-bearing smelter byproducts may undergo dissolution reactions followed by one of many pathways including reprecipitation into new solid phases, sorption to organic and inorganic soil constituents, colloid-facilitated transport, and uptake by plants and organisms. The purpose of this study was to use micro-XAS and micro-XRF spectroscopies to determine the speciation of Zn in the soils of Blue Mountain.

EXPERIMENT

This study employed micro-XANES and micro-XRF spectroscopies on Zn-contaminated soils at beamline 10.3.2 at the Lawrence Berkeley National Lab Advanced Light Source (LBNL-ALS) [3]. Surface (< 5 cm) and subsurface(< 500 cm) soil samples were collected, air-dried, embedded in an acrylic resin (LR-White resin), and polished into 50 μm thin sections. Elemental maps were collected for Fe, Mn, and Zn over an area of 1 mm^2 with 5 μm steps. Using the generated map, XANES spectra were collected on "hot spots" (areas of highest metal concentration) 100 eV below the absorption edge to 500 eV beyond the absorption edge with increments varying from 0.05 to 10 eV. Spectra were collected on several Zn-bearing mineral phases and for Zn sorbed on reference oxides and clay minerals to aid in Zn speciation.

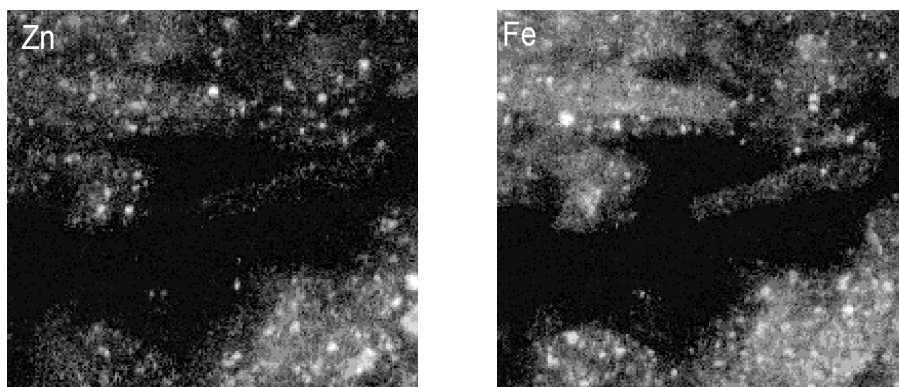


Fig. 1 Gray scale elemental map of Zn and Fe in surface sample, 1mm² area.
The white areas indicate the highest concentration of the element.

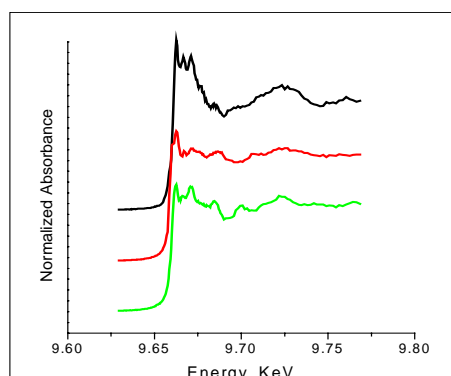


Fig. 2 Zn XANES spectra from selected regions in the surface sample.

RESULTS AND CONCLUSIONS

Comparison of the Zn XANES spectra to reference Zn-bearing materials indicate that in the organic-matter rich surface soil the Zn “hot spots” are a combination of Zn-sulfide (sphalerite) and Zn-Fe oxide mineral phases (franklinite) (Fig. 1). This difference in Zn speciation in the surface soil occurred in an area of only a few hundred square microns, a difference that would not be detected using standard XAS. The elemental map shows an association of Zn with Fe (Fig. 2). Data for the subsurface samples are not presented, however the XANES indicate that Zn is predominately present as an adsorbed complex to a Mn oxide (birnessite). The elemental map of the subsurface sample shows Zn associated with Mn. X-ray fluorescence data shows Zn is associated with Fe in the surface sample and with Mn in the subsurface sample. This difference in Zn speciation in the surface and subsurface soils suggests weathering of the primary Zn mineral phases in the surface sample, followed transport and sorption processes in the subsurface sample.

REFERENCES

1. D.B. Hunter and P.M. Bertsch, J. Radioanal. Nucl. Chem. **234** (1-2) 237 (1998).
2. W. Yun, S.T. Pratt, R.M. Miller, Z. Cai, D.B. Hunter, A.G. Jarstfer, K.M. Kemner, B. Lai, H.-R. Lee, D.G. Legnini, W. Rodrigues, and C.I. Smith. J. Synchrotron Rad. **5** 1390 (1998).
3. A.A. MacDowell, R. Celeste, C.-H. Chang, K. Franck, M.R. Howells, S. Lockin, H.A. Padmore, J.R. Patel, R. Sandler. Proc. SPIE **3152** 126 (1997).

ACKNOWLEDGEMENTS

This work was supported by a National Science Foundation Graduate Fellowship and the DuPont Company.

Principal investigator: Donald L. Sparks, Department of Plant and Soil Sciences, Townsend Hall, University of Delaware, Newark, DE, 19711. 302-831-2532. Email: dlsparks@udel.edu